

TRANSLATION:

(19) Federal Republic of Germany

P A T E N T

(12) Exclusion Patent

(11) Document No.: DD 294 703 A5

(51) Intl. Cl.⁵: C 04 B 41/68

Granted pursuant to § 17 Paragraph 1 of the Patent Law of the German Democratic Republic of October 27, 1983 in accordance with the corresponding agreements in the Unification Treaty

GERMAN PATENT OFFICE

Published in the version submitted
by the applicant.

(21) File No.: DD C 04 B / 341 165 4

(22) Application Date: May 31, 1990

(44) Publication Date of Examined
Document on Which Grant Has
Taken Place on or Before Said Date: October 10, 1991

(71) Applicant: Energiewerke Schwarze Pumpe AG,
O-7610 Schwarze Pumpe, DE

(72) Inventor(s): Kleber, Friedmar, Graduate Mineralogist;

Kallmeier, Knut;

Chudak, Hans-Rainer, Graduate Chemist;

Hinze, Detlef, Graduate Engineer;

Enders, Heinz;

Findeisen, Hartmut;

Nitz, Wolfgang;

Knölle, Gabriele, Graduate Chemist, DE

(73) Grantee(s):

Energiewerke Schwarze Pumpe AG, O-7610
Schwarze Pumpe;

VEB Feuerfestwerk Wetro, O-8601 Wetro;

VEB Chemiewerk Bad Köstritz, O-6504 Bad
Köstritz;

Brennstoffinstitut Freiberg, O-9200 Freiberg, DE

(54) Title of the Invention:

PROTECTIVE COATING FOR THE SILICON CARBIDE REFRACTORY
LINING OF HIGH-PRESSURE FIXED-BED GASIFIERS

(55) Keywords:

Protective coating; silicon carbide; fixed-bed high-pressure gasifier; suspension; silicasol;
alumina; α -Al₂O₃; amorphous SiO₂; mullite matrix; thermal conductivity

(57) Abstract:

The present invention concerns a protective coating for a silicon carbide lining of high-pressure fixed-bed gasifiers. In accordance with the invention, after a conventional silicon carbide lining has been installed in the high-pressure fixed-bed gasifier, it is treated by repeated spreading or spraying with a suspension of 40-65% silicasol with 30% SiO₂ and 35-60% finely ground alumina (half-value particle size 2.5 μ m) with an α -Al₂O₃ fraction of 85-95%, but if shaped bricks are used, the treatment can also be carried out before the installation of the lining. The silicasol penetrates the silicon carbide lining and reduces its porosity. A dense, alumina-rich, strongly adherent protective coating forms on the surface. This ensures good thermal conductivity of the refractory lining over a long period of time.

CLAIM

Protective coating for the silicon carbide lining of high-pressure fixed-bed gasifiers, produced by repeated spreading or spraying or impregnation of mullite-bonded or clay-bonded silicon carbide bricks before or after their installation in the high-pressure fixed-bed gasifier, characterized by the fact that the suspension consists of 35-65% silicasol with 30% SiO_2 and 35-65% finely ground alumina with an $\alpha\text{-Al}_2\text{O}_3$ fraction of 85-95%, which is ground to a high degree of fineness (half-value particle size around $2.5\ \mu\text{m}$) by standard grinding equipment used in the ceramics industry.

Scope of the Invention

The invention concerns the refractory ceramic inner lining of high-pressure fixed-bed gasifiers, in which the solid fuel lignite is gasified by a gasifying agent under a pressure of $< 3.5\ \text{MPa}$ and temperatures of $< 1,300^\circ\text{C}$. In particular, the invention concerns the protection of the refractory material of high-pressure fixed-bed gasifiers.

Characterization of the Prior Art

It is well known that, in the gasification of solid fuels in high-pressure fixed-bed gasifiers, the maximum temperature in the oxidation zone is limited by the softening point or melting point of the inorganic components of the fuel. The maximum temperature is set by the steam/oxygen ratio. The lower the softening point or melting point is, the higher the steam/oxygen ratio must then be. This has a negative effect on the economy of the process. Therefore, the hottest possible operation of the high-pressure fixed-bed gasifier, right at the limit

of slagging, is advantageous. Slag accretions can be all the more reliably avoided, the lower the surface temperature of the inner wall of a high-pressure fixed-bed gasifier is. It is also well known that at a low softening point of the inorganic components of the fuel and at the same time a low steam/oxygen ratio, the lining of the high-pressure fixed-bed gasifier is vigorously attacked, and disruptive slag accretions form at the same time. Furthermore, it is well known that there are only a few refractory materials that can withstand these stresses for prolonged periods of time. These materials include high-grade SiC bricks. The very good thermal conductivity of these SiC bricks, combined with cooling of the inner jacket of the high-pressure fixed-bed gasifier, results in good heat dissipation, which hinders the melting process of the inorganic components of the fuel and the reaction with the lining material. The durability of presently used clay-bonded silicon carbide bricks with an SiC content of 65% is not satisfactory at present, since slag formation occurs on the wall between the lining material and the coal ash, e.g., by infiltration, and is also associated with the well-known corrosion phenomena behind the lining.

The relatively high porosity of the SiC bricks for lining high-pressure fixed-bed gasifiers is a disadvantage, because this increases the chance of reaction between the coal ash and the fluxes of the bricks. The conversion of the SiC to SiO₂ is accompanied by a loss of strength due to loosening of the structure and by a decrease in thermal conductivity. The resulting increase in temperature on the inner wall of the high-pressure fixed-bed gasifier promotes chemical attack by the coal ash. This leads to slag accretions on the inner wall, which cause narrowing of the cross section of the high-pressure fixed-bed gasifier, with the result that the high-pressure fixed-bed gasifier must be taken out of service prematurely. It is well known that various economic patents have already proposed solutions for increasing the economy of high-pressure fixed-bed

gasifiers by improving the elimination of heat, but these have not led to satisfactory results. For example, DD WP 227975 proposed that thermally conductive cement of a well-known composition be used as the bonding agent for lining high-pressure fixed-bed gasifiers. Due to the high porosity (about 45%) of the thermally conductive cement, corrosive media penetrated the pores. Increased corrosion occurred on the inner jacket due to the contact of these media with the lining of the generator.

Objective of the Invention

The objective of the invention is to discover a means of protecting the silicon carbide lining of high-pressure fixed-bed gasifiers to prevent slag accretions even at low steam/oxygen ratios by improving heat transfer from the inner wall to the water-cooled inner jacket of the high-pressure fixed-bed gasifier. The economy of the high-pressure fixed-bed gasifier is to be improved by

- increasing the availability of the high-pressure fixed-bed gasifier:
- reducing the need for gasification steam:
- reducing the maintenance work: and
- achieving savings of high-grade refractory materials.

Description of the Nature of the Invention

The objective of the invention is to develop a protective coating for the ceramic lining of high-pressure fixed-bed gasifiers, which diminishes the disadvantages of the SiC bricks that are used and thus improves the economics of the high-pressure fixed-bed gasifiers by reducing the steam/oxygen ratio.

In accordance with the invention, after a conventional silicon carbide lining has been installed in the high-pressure fixed-bed gasifier, it is treated by repeated spreading or spraying with a suspension of 40-65% silicasol with 30% SiO_2 and 35-60% finely ground alumina (< 0.04 mm) with an $\alpha\text{-Al}_2\text{O}_3$ fraction of 85-95%, but if shaped bricks are used, the treatment can also be carried out before the installation of the lining. The silicasol penetrates the silicon carbide lining and reduces its porosity. A dense, alumina-rich, strongly adherent protective coating forms on the surface. This result is obtained, because, on the one hand, due to the relatively high degree of calcining, the alumina guarantees that the protective coating does not become permeable under high thermal loads due to shrinkage processes of the alumina but, on the other hand, is so reactive, due to the still remaining fraction of transition alumina and its extreme fineness, that a stable mullite matrix is formed with the amorphous SiO_2 of the silicasol starting at temperatures of only 780°C , and the excess alumina is tightly bound in the matrix. This special alumina can be very finely ground (half-value particle size $2.5\ \mu\text{m}$) with standard grinding equipment used in the ceramics industry, such as tumbling mills or tube mills, due to the well-defined fraction of $\alpha\text{-Al}_2\text{O}_3$ and a favorable crystalline state, which is based on the necessary manner of carrying out the calcination to achieve this $\alpha\text{-Al}_2\text{O}_3$ content. The protective coating, which is so thin that it does not hinder the elimination of heat from the gasification space to the water-cooled inner jacket, constitutes oxidation protection for the silicon carbide, so that the good thermal conductivity of the refractory lining is maintained for a long period of time. Due to the associated low temperature on the inner wall of the high-pressure fixed-bed gasifier, the reaction of the ash with the refractory lining is hindered. Furthermore, the dense $\alpha\text{-Al}_2\text{O}_3$ -rich coating itself hardly reacts at all with the coal ash and, in addition, prevents direct contact between ash and SiC material. The solution in accordance with the invention makes it possible to increase the

reaction temperature of the process by reducing the steam/oxygen ratio with well-known advantages without the gasification process being hindered or interfered with by slag accretions on the inner wall of the high-pressure fixed-bed gasifier.

Embodiment

The solution in accordance with the invention will now be explained on the basis of an embodiment. A high-pressure fixed-bed gasifier is lined with mullite-bonded silicon carbide bricks. Before the high-pressure fixed-bed gasifier is placed in operation, a suspension of 65% silicasol with 30% SiO₂ and 35% finely ground alumina (half-value particle size 2.5 μ m) with an α -Al₂O₃ content of 85-95% is repeatedly applied to the refractory lining by spreading. When the high-pressure fixed-bed gasifier is heated up, a strong, mullite-bound alumina coating forms, which protects the silicon carbide of the refractory material from oxidation and prevents direct contact between coal ash and the SiC lining. This makes it possible to increase the reaction temperature of the process by reducing the steam/oxygen ratio to < 6.5 kg/m³ (STP) with well-known advantages without slag accretions forming on the shotcreted layer of the high-pressure fixed-bed gasifier.